Advanced *In Situ* Diagnostic Techniques for Battery Materials

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DOE Vehicle Technologies Office

ES059

BROOKHAVEN NATIONAL LABORATORY

Overview

Timeline

- ▣ Start: 10/01/2015
- ▣ Finish: 09/30/2018

Barriers addressed

- To reduce the production cost of a PHEV battery
- Li-ion and Li-metal batteries with long calendar and cycle life
- Li-ion and Li-metal batteries with superior abuse tolerance

Budget

- ▣ Funding received in FY16

  DOE: $600k

- ▣ Funding received in FY17

  DOE: $600k

Collaborators

- University of Wisconsin at Milwaukee
- Drexel University
- University of Maryland at College Park
- Lawrence Berkeley National Laboratory (LBNL)
- Argonne National Lab. (ANL)
- Pacific Northwest National Lab. (PNNL)
- Johnson Control Inc.

- Beijing Institute of Physics, Chinese Academy of Sciences
- Beijing Institute of Technology

Relevance and Project Objectives

✓ ***Diagnostic studies to understand the structural changes of cathode materials during high rate charge-discharge cycles (to improve the rate capability of electrode materials for Li-ion batteries).***

- ➥ to investigate the structural changes of various cathode materials, especially the NMC materials cycled at different rates, especially at high rate cycling.
- ➥ to search new approaches to improve the high rate capability of cathode materials including optimize the content of transition metal elements, as well as doping and surface modification techniques.
- ➥ to provide valuable information about how to design cathode materials with better rate capability for xEV applications.
- ➥ to develop new *in situ* diagnostic techniques to study the high rate capability cathode materials.

✓ ***Diagnostics study to understand the voltage and capacity fading mechanism during multiple cycling for high energy density materials (to increase the energy density and cycling life of Li-ion batteries)***

- ➥ to develop in situ diagnostic techniques with surface and bulk sensitivity to improve the calendar and cycle life of batteries by studying the mechanism of capacity, voltage, and power fading of Li-ion battery.
- ➥ to develop multi scale imaging diagnostic techniques such as TEM , nano-probe, as well as TXM imaging, and combining them together with spectroscopy (x-ray absorption) to improve calendar and cycle life of batteries by studying the mechanism of capacity, voltage, and power fading of Li-ion battery.

✓ ***Diagnostics study aimed to improve the safety characteristics of batteries.***

- ➥ to develop in situ diagnostic techniques with surface and bulk sensitivity to study the thermal stability of cathode materials at different charged states and cycling conditions and history aimed to improve the thermal stability and safety characteristics of Li-ion batteries.

✓ ***Diagnostics study of electrode materials with lower cost potential.***

Milestones

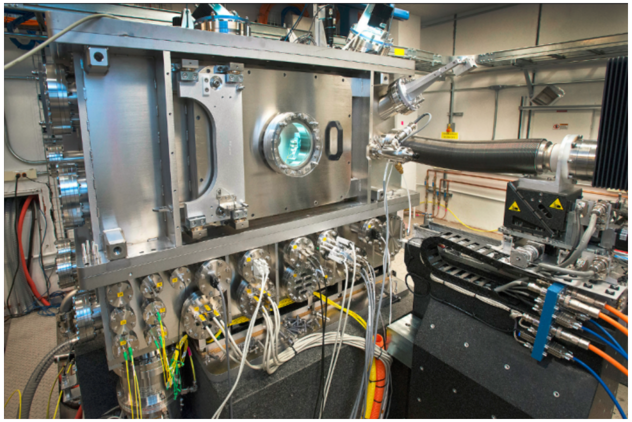
Month/Year	Milestones
Dec/2016	Complete the structure studies of $Li_2Ru_{0.5}Mn_{0.5}O_3$, as a model compound for Li and Mn rich (LMR) high energy density cathode materials using pair distribution function (PDF) to correlate the voltage and capacity fading with micro-structural defects in this type of materials. ➥ *Completed.*
Mar/2017	Complete the structure studies $Li_2Ru_{0.5}Mn_{0.5}O_3$, as a model compound for Li and Mn rich (LMR) high energy density cathode materials using scanning transmission electron microscopic (STEM) to correlate the voltage and capacity fading with micro-structural defects in this type of materials. ➥ *Completed.*
Jun/2017	Complete the XRD and XAS studies of $Li_2Ru_{0.5}Mn_{0.5}O_3$cathode material samples with different cycle history (charge and discharge limit and cycle numbers). ➥*On schedule.*
Sep/2017	Complete the structure studies of $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$ for Li and Mn rich (LMR) high energy density cathode materials using scanning transmission electron microscopic (STEM) to correlate the voltage and capacity fading with micro-structural defects in this type of materials. ➥ *On schedule.*

Approaches

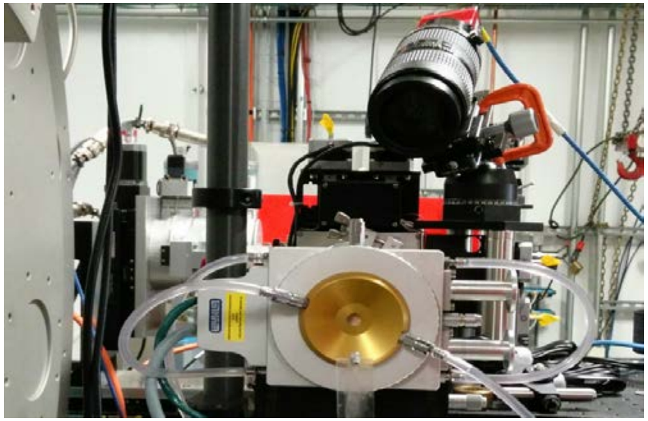
- Using nano-probe beamline at NSLSII to study the elemental distribution of new solid electrolyte materials for Li-ion and Na-ion batteries
- Using pair distribution function (PDF) techniques to study the effects of multiple cycling for $Li_2Ru_{0.5}Mn_{0.5}O_3$ cathode material with and without pre-lithiation (Micro structural defects were intentionally generated) to improve the performance of high energy density materials.
- Using high resolution transmission electron microscopy (TEM) to obtain multiple dimensional (3D + elemental, valence state, and time) mapping of new cathode materials for advanced Li-ion batteries.
- Using transmission x-ray microscopy (TXM) to do multi dimensional mapping of cathode materials
- Using A combination of time resolved X-ray diffraction (TR-XRD) and mass spectroscopy (MS), together with *in situ* soft and hard X-ray absorption (XAS) during heating to study the thermal stability of the electrode materials
- Using *in situ* XRD and XAS, to study the new concentration gradient cathode materials to improve the cycle life of Li-ion batteries
- Using quick x-ray absorption spectroscopy and time resolved x-ray diffraction techniques to study the kinetic properties and the structural changes of $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material during high rate charge process to improve high rate capability of Li-ion batteries.

Approach: Elemental mapping using Nano-probe beamline and PDF studies using XPD beamline at NSLSII (BNL)

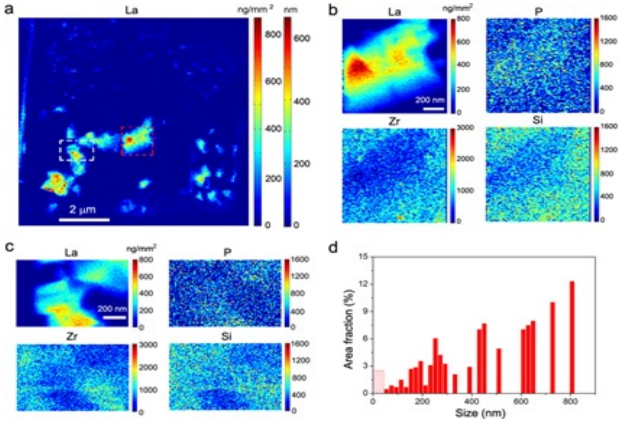
The photo of Nano-probe x-ray microscope
At Hard x-ray Nano-probe beamline (HXN) at NSLSII



The photo of X-ray Powder Diffraction beamline (XPD) at NSLSII for in situ structural studies for Li-ion battery electrode materials.

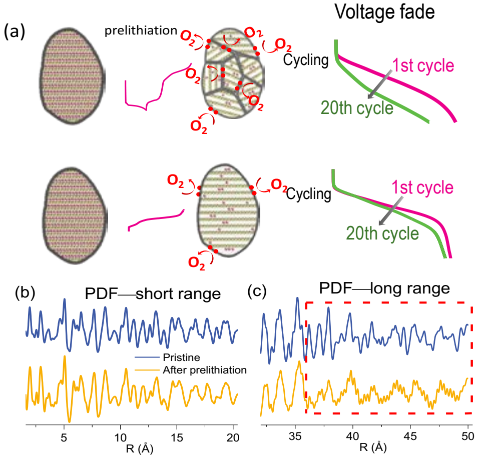


The images of elemental distribution for a novel solid-state electrolyte ceramic material sample collected at Hard x-ray Nano-probe beamline (HXN) at NSLSII



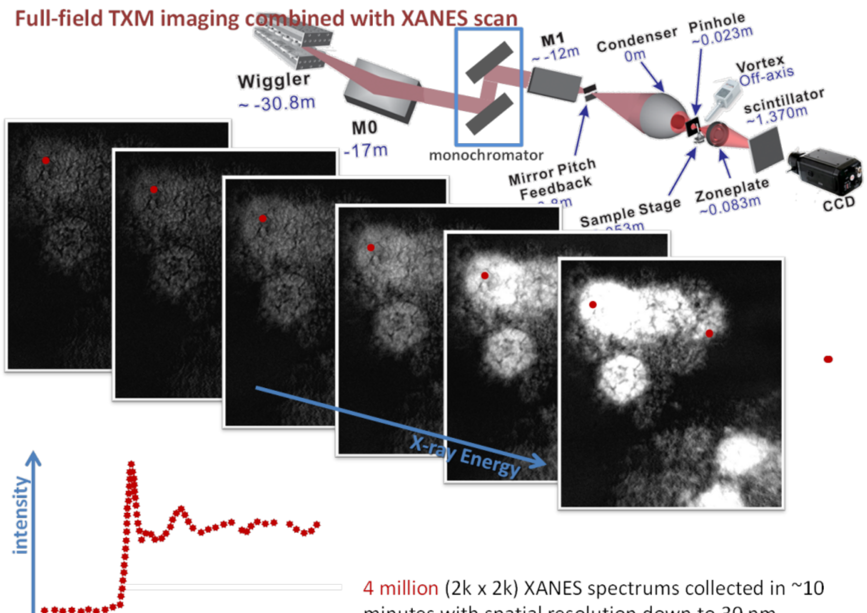
Z. Zhang et al, Adv. Energy Mater, 2016.

PDF results using XPD beamline at NSLSII to study the effects of multiple cycling for $Li_2Ru_{0.5}Mn_{0.5}O_3$ cathode material with and without pre-lithiation (Micro structural defects were intentionally generated).

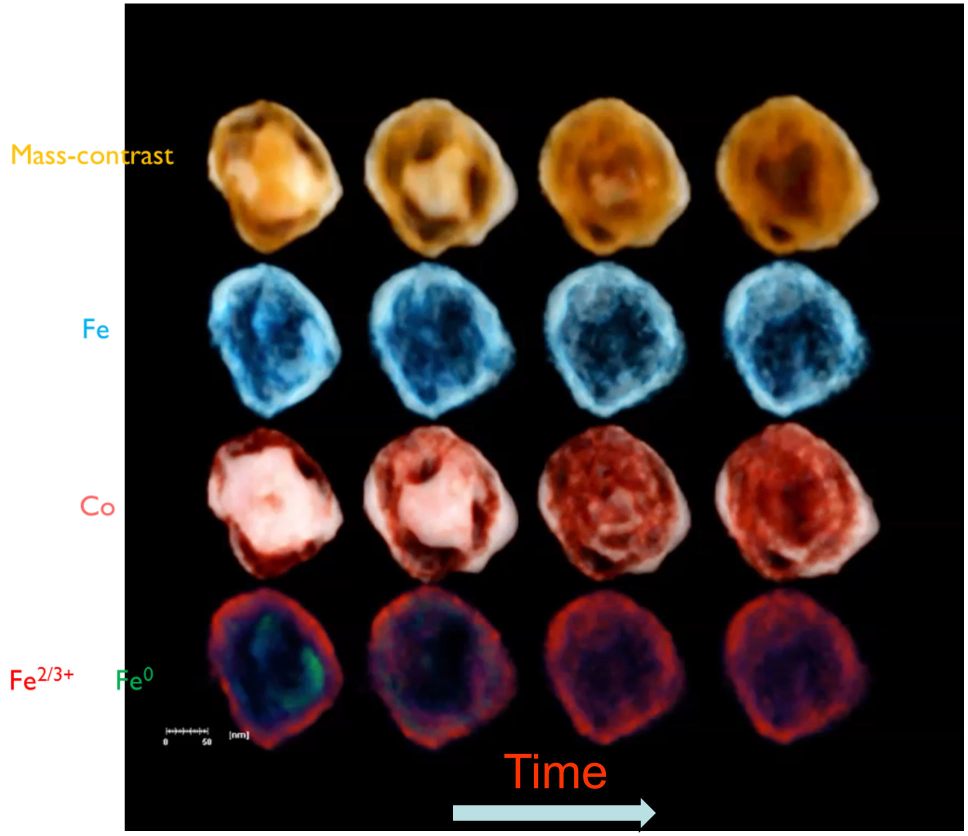


E. Hu et al, Nano Letter 2016.

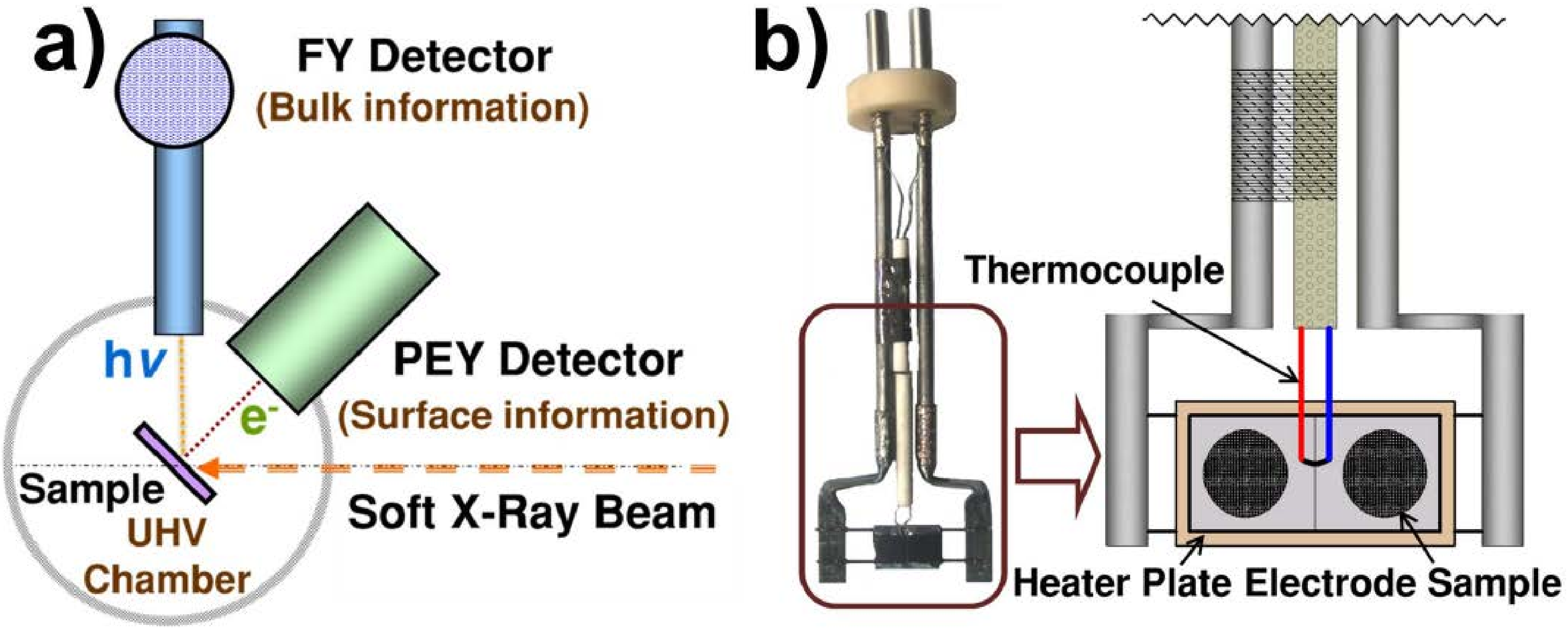
Approach: Using TXM (with Yijin Liu at SLAC) and TEM (with Huolin Xin at BNL) to do multiple dimensional (3D + elemental, valence state, time) mapping and spectroscopy (XAS)



4 million (2k x 2k) XANES spectrums collected in ~10 minutes with spatial resolution down to 30 nm.



Approach: Thermal stability study using in situ soft X-ray XAS



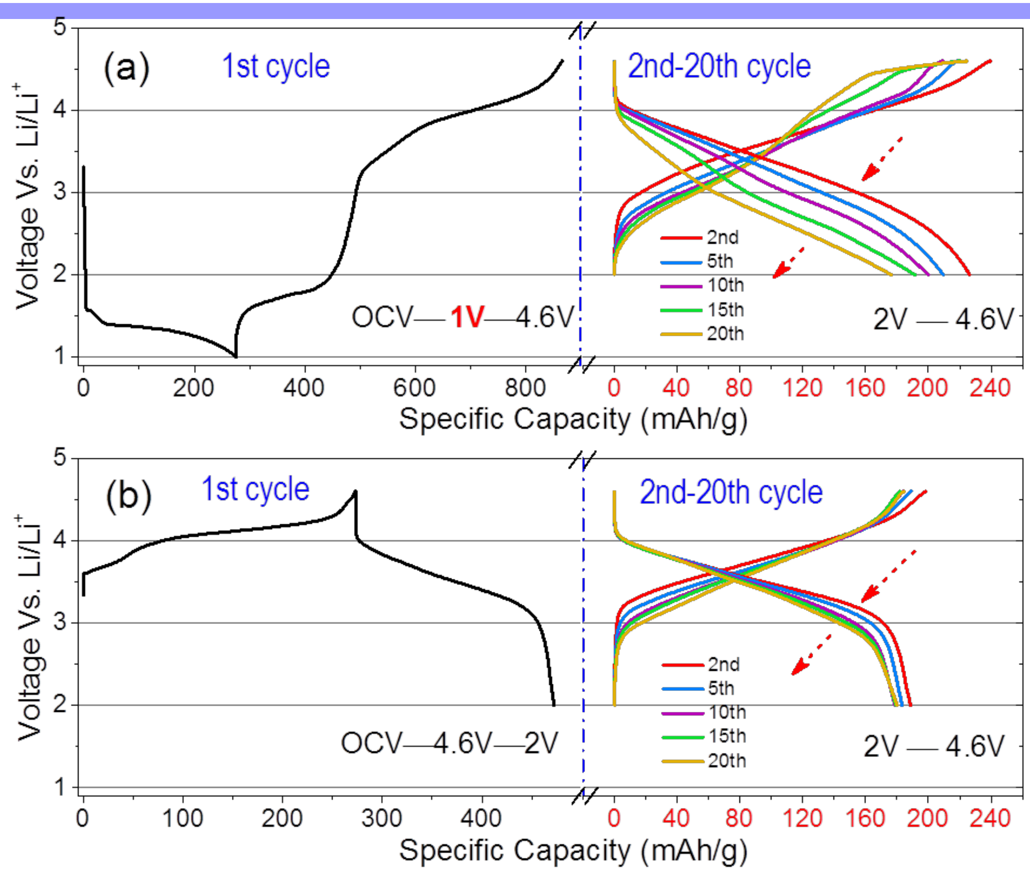
Schematic diagram of (a) in situ soft XAS experimental setup and (b) sample heater with heating stage for in situ soft XAS experiment.

The partial electron yield (PEY) measurement in soft XAS gives information about surface properties (up to ~5 nm), while the fluorescence yield (FY) measurements probes bulk properties (up to ~300nm).

Technical Accomplishments and Progress

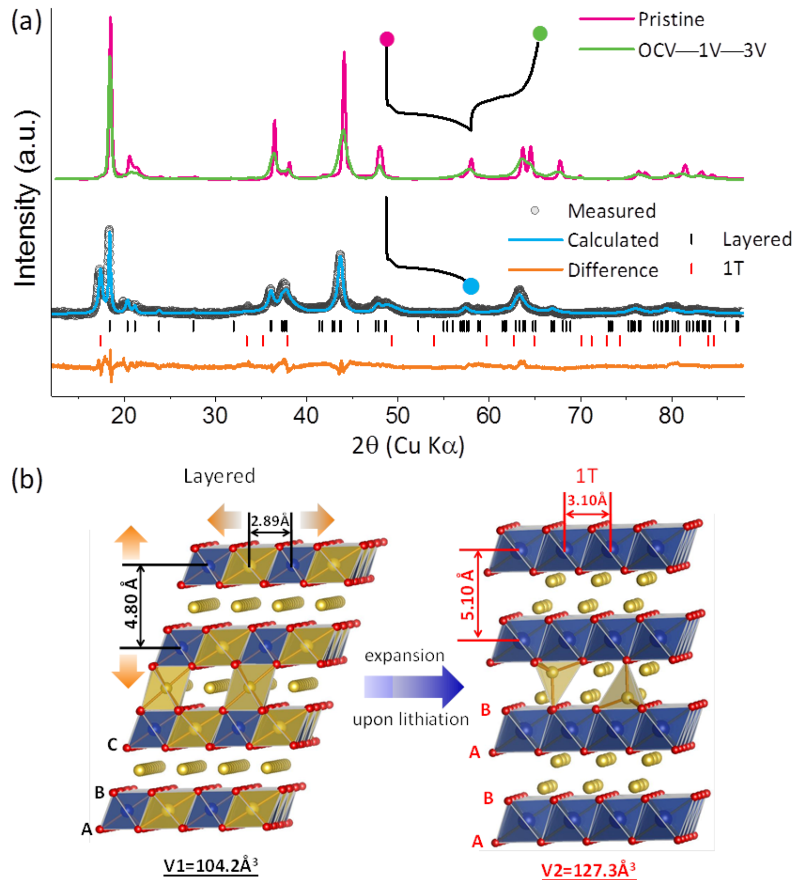
- By collaborating with Dr. Yijin Liu at Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, and Prof. Xiqian Yu and Prof. Hong Li at Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, the studies of $Li_2Ru_{0.5}Mn_{0.5}O_3$, as a model compound for Li and Mn rich (LMR) high energy density cathode materials have been carried out using TXM and pair distribution function (PDF) to correlate the voltage and capacity fading with micro-structural defects in this type of materials The results were published on *Nano Energy*
- By collaborating with Dr. Huolin Xin at BNL, Z-contrast scanning transmission electron microscopic (STEM) has been used to study the microstructural defects created by prelithiation through comparison of the images between pristine and prelithiated $Li_2Ru_{0.5}Mn_{0.5}O_3$. The effects of such microstructural defects on the voltage fading during cycling were studied and the results were published on *Nano Letters*
- By collaborating with beamline scientists at X-ray powder diffraction (XPD) and Hard x-ray nano-probe (HXN) beamlines at NSLSII, new *in situ* and *ex situ* studies of battery materials using the unique capability of these two beamlines have been designed and carried out.

The voltage fading is accelarted during cycling for prelithiated $Li_2Ru_{0.5}Mn_{0.5}O_3$



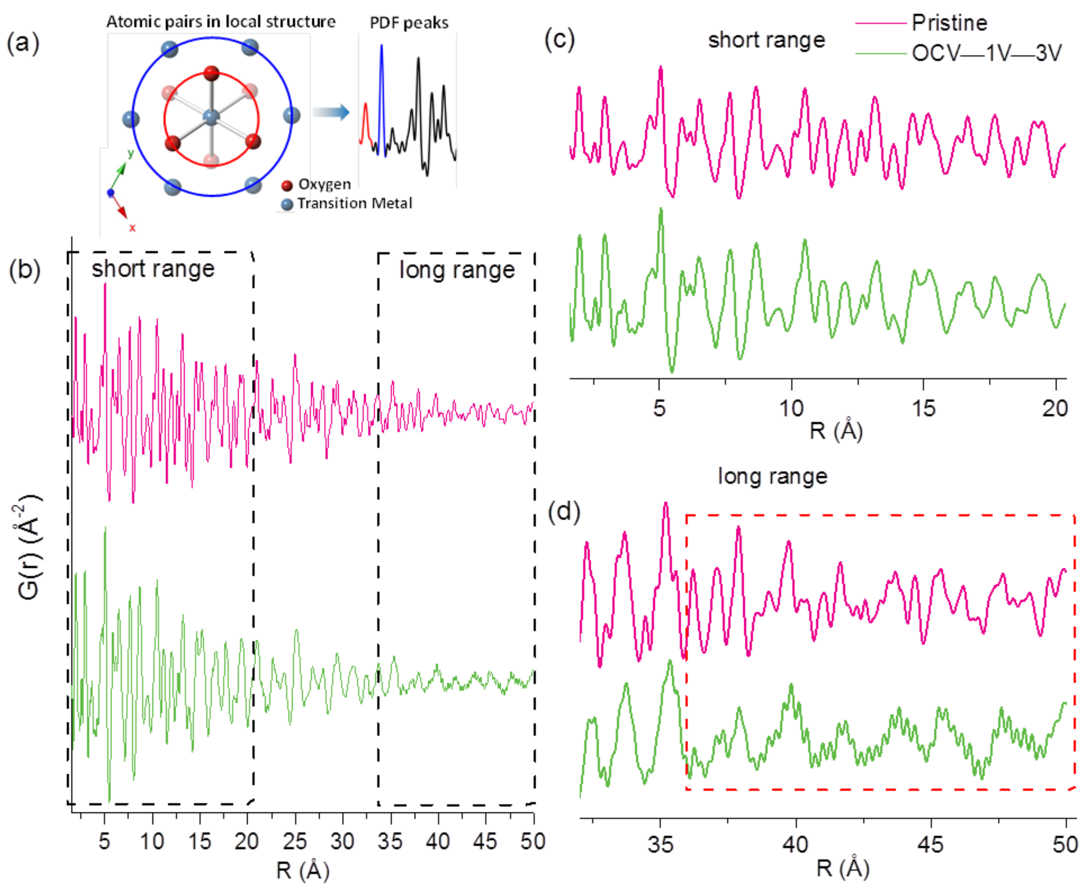
Electrochemical performances of (a) prelithiated $Li_2Ru_{0.5}Mn_{0.5}O_3$which is first discharged to 1 V and then charged to 4.6 V, followed by cycling between 2V and 4.6 V; (b) normally cycled $Li_2Ru_{0.5}Mn_{0.5}O_3$ which is directly cycled between 2 V and 4.6 V without discharging first. The current used is C/8, corresponding to 0.07 mA/cm^2 in all cases.

Ex situ XRD patterns and illustrations of unit cell expansion after Prelithiation for $Li_2Ru_{0.5}Mn_{0.5}O_3$



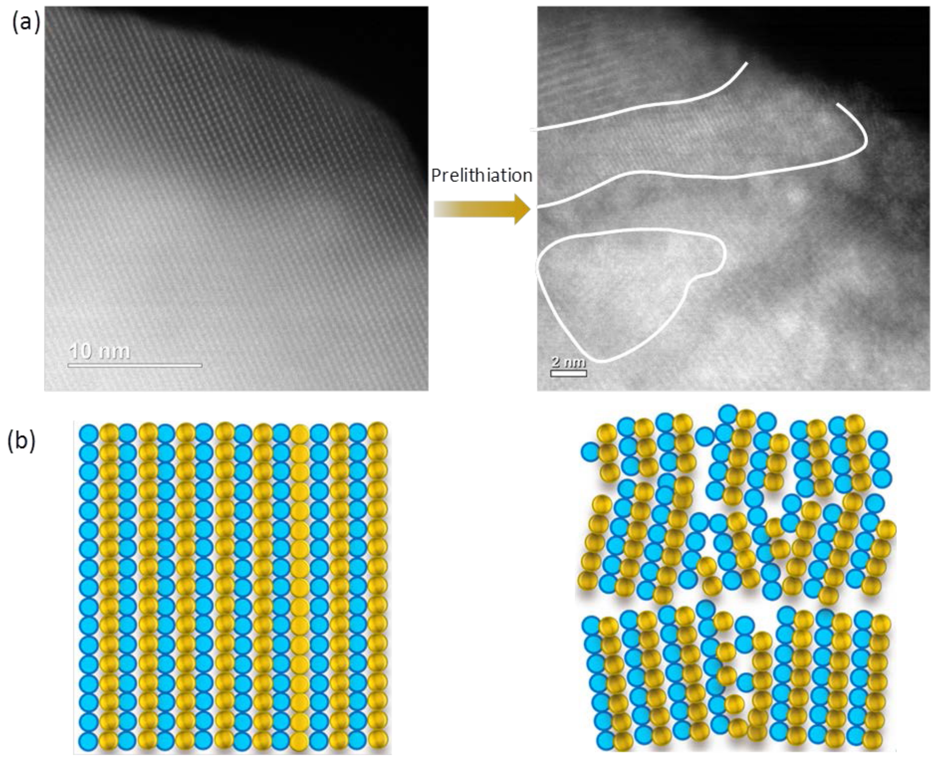
(a) *Ex situ* XRD studies of $Li_2Ru_{0.5}Mn_{0.5}O_3$ during prelithiation process. The upper panel shows XRD patterns of the pristine sample and the sample that is first discharged to 1 V and then charged to 3 V (OCV—1V—3V). The lower panel shows results from Rietveld refinement of the sample discharged to 1 V (OCV—1V), with experimental data shown in dotted circles, fitted data shown in blue, and difference shown in orange. (b) Structure illustrations of layered phase and 1T phase, showing volume expansion during phase transition.

PDF results showing that the long-range ordering in prelithiated $Li_2Ru_{0.5}Mn_{0.5}O_3$ is significantly deteriorated comparing with the pristine one



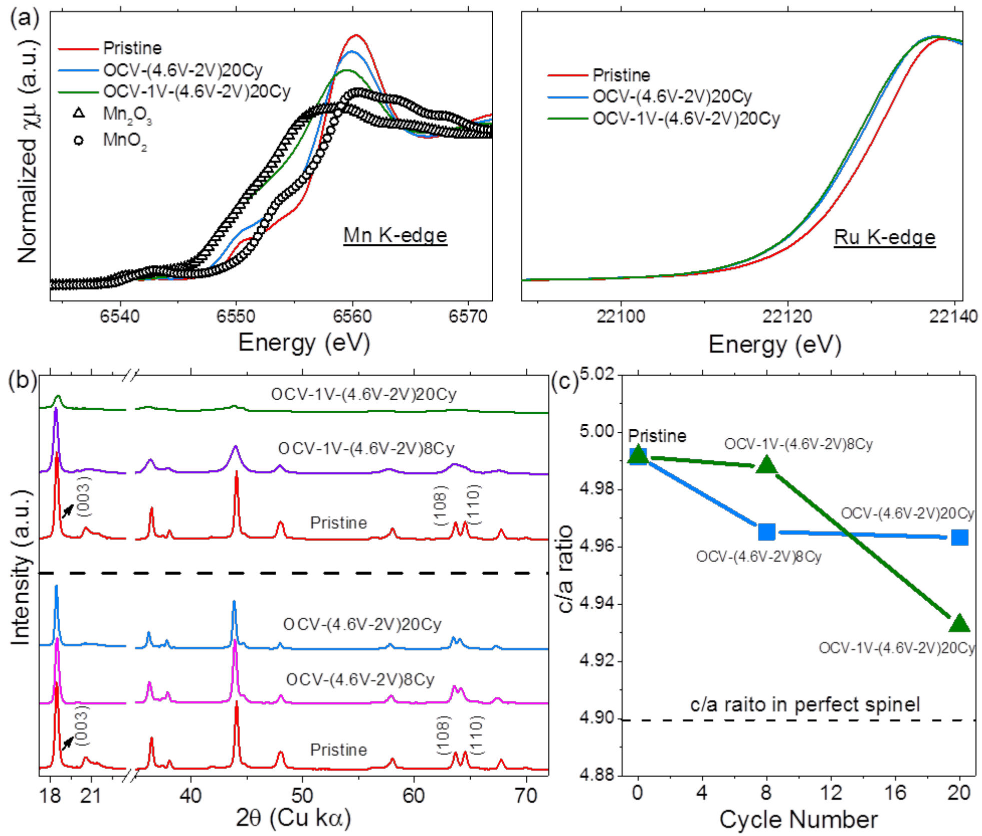
(a) Illustration of PDF showing that peaks correspond to characteristic bond lengths. (b) *Ex situ* PDF results of pristine sample and “OCV—1V—3V” sample (c) zoomed in data on the short range region of ex situ PDF data and (d) zoomed in data on the long range region of *ex situ* PDF data.

STEM images of pristine and prelithiated $Li_2Ru_{0.5}Mn_{0.5}O_3$ With illustration of the microstructural defects created by prelithiation



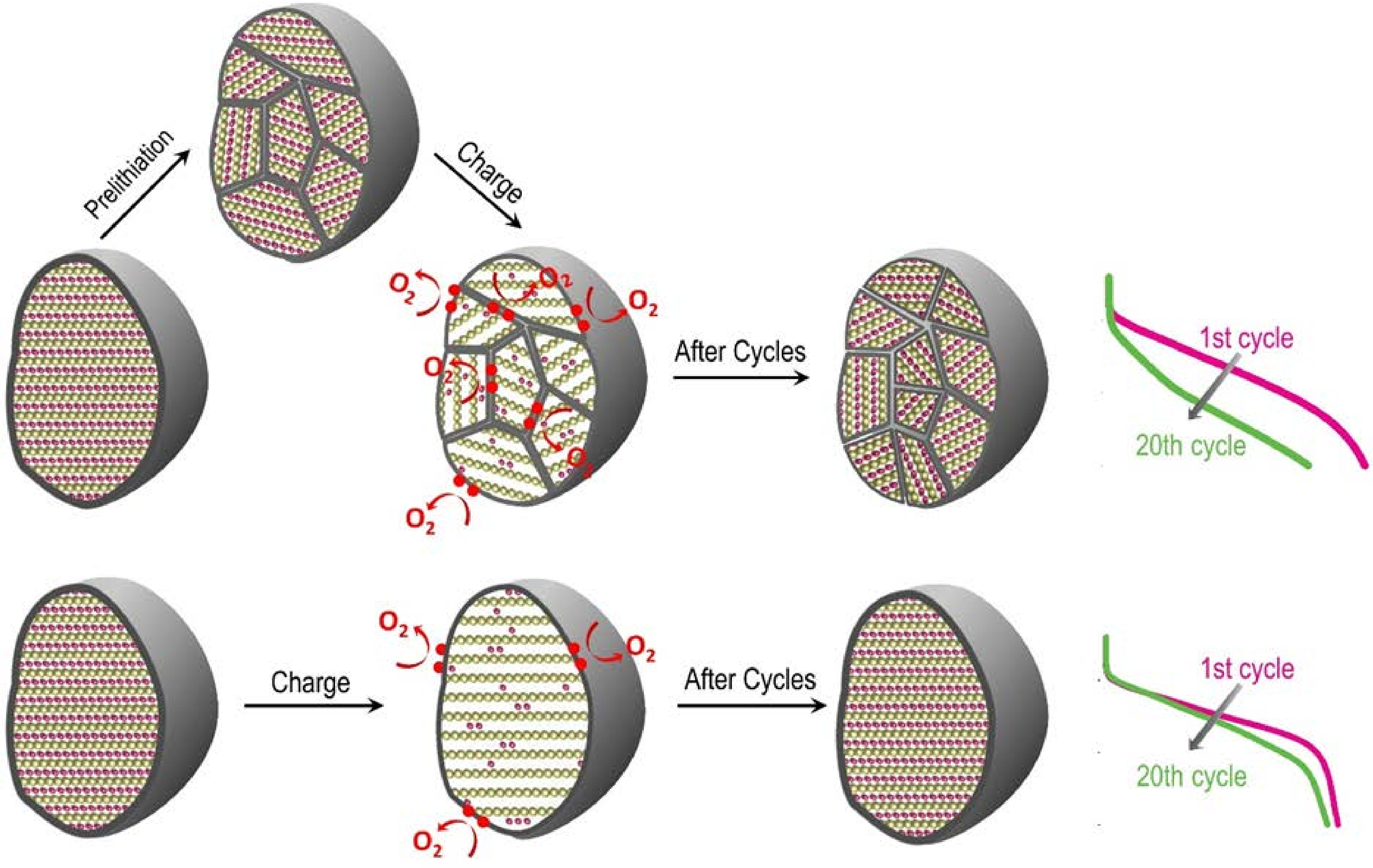
(a) Z-contrast scanning transmission electron microscopic (STEM) images of pristine sample and "OCV—1V—3V" sample. In the "OCV—1V—3V" sample, a few selected domains are circled out by the white lines. (b) Illustration of the microstructure change brought by prelithiation process.

Ex situ Mn K-edge and Ru K-edge XAS and XRD patterns for prelithiated $Li_2Ru_{0.5}Mn_{0.5}O_3$ samples with different cycling history



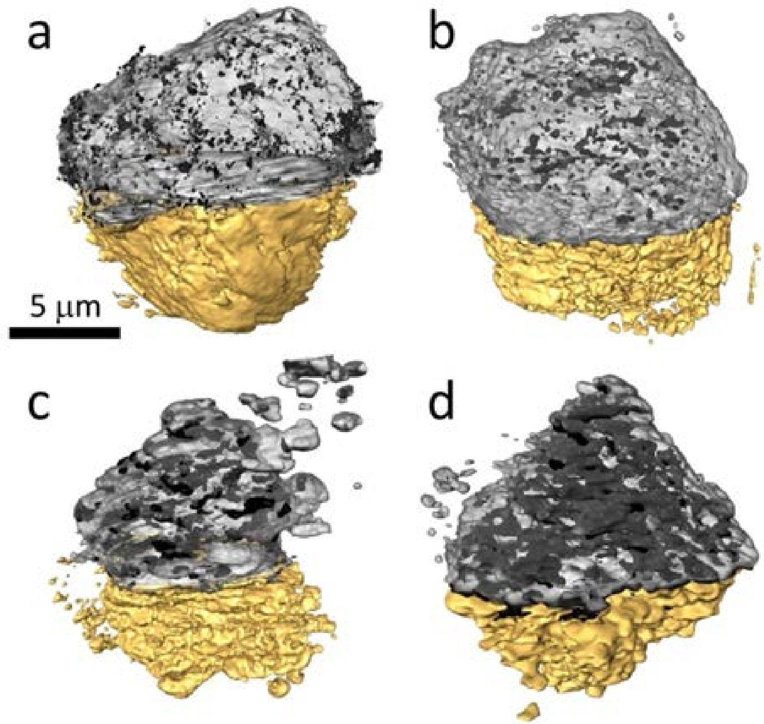
(a) *ex situ* Mn K-edge and Ru K-edge XAS data of pristine sample, sample normally cycled 20 times and sample cycled 20 times but first prelithiated, with references of Mn_2O_3 and MnO_2 shown. (b) *Ex situ* XRD patterns of two cases (with (003), (108) and (110) peaks indexed according to the space group $R\bar{3}m$): pristine sample, cycled 8 times and cycled 20 times for the normally cycled case (the part below the dash line); pristine sample, cycled 8 times and cycled 20 times for the prelithiated case (the part above the dash line). (c) The ratio between lattice parameter *c* and lattice parameter *a* as a function of cycle numbers. The dash line shows the *c*/*a* ratio in perfect spinel.

Illustration of prelithiation-induced micro-structural defects as well as smaller crystallite size and their effect on voltage fade for $Li_2Ru_{0.5}Mn_{0.5}O_3$



Xiao-Qing Yang *et. al*., Nano Lett., 2016, 16 (10), pp 5999–6007, DOI: 10.1021/acs.nanolett.6b01609

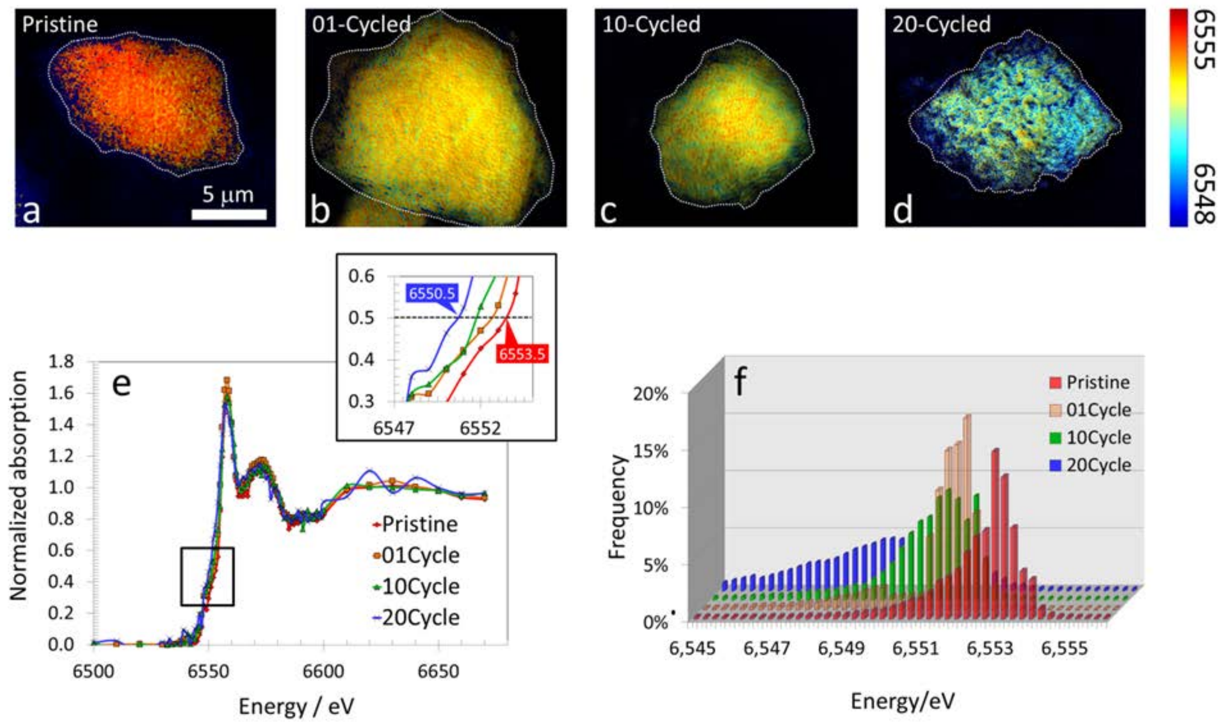
The TXM 3D visualization of the $Li_2Ru_{0.5}Mn_{0.5}O_3$ particles after different number of cycling



Reconstructed TXM 3D visualization of the particles at a) pristine, b) 01-cycled, c) 10-cycled, and d) 20-cycled. The internal pore space (black) develops from isolated voids into large and interconnected network.

Yahong Xu *et. al*., ", Nano Energy, Volume 28, October 2016, DOI: 10.1016/j.nanoen.2016.08.039

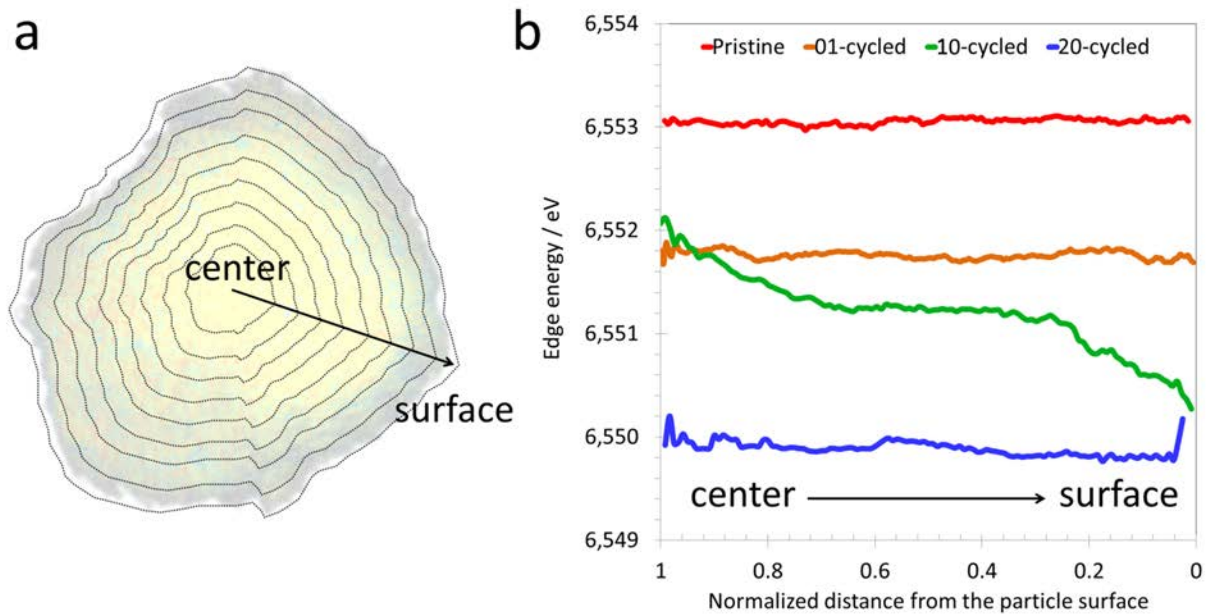
2D nanoscale mapping of the distribution of the Mn oxidation states in particles with different cycling history for $Li_2Ru_{0.5}Mn_{0.5}O_3$



2D nanoscale mapping of the distribution of the Mn oxidation states in particles with different cycling history. Panels a) through d) show that the overall Mn oxidation state is reduced upon cycling. Panel e) shows the bulk XANES of Mn for the particle. Panel f) shows the histogram of the Mn edge shift maps shown in panel a) to d).

Yahong Xu *et. al*., ", Nano Energy, Volume 28, October 2016, DOI: 10.1016/j.nanoen.2016.08.039

Evaluation of the depth dependency of Mn oxidation state distribution for $Li_2Ru_{0.5}Mn_{0.5}O_3$



Evaluation of the depth dependency of Mn oxidation distribution Panel a) shows schematically how the pixels are regrouped and the shell layers are identified for the evaluation of the depth dependency distribution of the Mn oxidation states. Panel b) shows the depth dependency of the Mn oxidation state in the four samples with different cycling history.

Yahong Xu *et. al.*, ", Nano Energy, Volume 28, October 2016, DOI: 10.1016/j.nanoen.2016.08.039

Response to 2015 reviewer's comments

This ES059 project was presented as a poster in the 2016 AMR review and no comments are provided in the 2016 VTO AMR Results Report. Therefore, response to 2015 reviewer's comments are used in this slide

Comments from 2015 AMR	Response
Blended $LiMn_2O_4$ (LMO)-$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode materials with different stoichiometric ratios have been studied. The discovered specific physicochemical processes in the LMO and NCM should be described clearly in the annual report, the reviewer urged.	The results of Blended $LiMn_2O_4$ (LMO)-$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode materials with different stoichiometric ratios had been published. The discovered specific physicochemical processes in the LMO and NCM have been clearly described in details in the annual report
The loss of key equipment at Brookhaven has led to a number of fruitful collaborations with laboratories and partners around the country, the reviewer observed, and the work has also engaged industry partners, which is key to transitioning diagnostic techniques out of the lab. Active engagement of the broader battery community is a key strong point of this work.	The collaborations with scientists at other synchrotron facilities such as APS at Argonne National Lab and SSRL at Stanford University and ALS at Berkeley National Lab. had been further strengthened. High quality data had been collected and scientific papers have been prepared or published. More industry partners have been contacted and broader collaboration with battery community are being developed
The reviewer recommended much more collaboration with other national laboratories, universities and battery companies working on novel materials or cells that meet DOE electric vehicle (EV) or plug-in hybrid electric (PHEV) goals..	More collaborations with other national laboratories, universities and battery companies working on novel materials to meet DOE electric vehicle (EV) goals have been developed. These institutions including ANL, PNNL, LBNL, ORNL, MIT, Drexel University, and Johnson Control

Collaborations with other institutions and companies

- Yale University
  Li-S batteries
- University of Maryland at College Park
  High energy density cathode materials for Li-ion batteries
- Drexel University
  Probing the mechanism of high capacitance anode materials of 2D titanium carbides
- Argonne National Lab. (ANL)
  In situ XRD and XAS study of high energy density Li_2MnO_3-$LiMO_2$ composite (LMR-NCM).
- Pacific Northwest National Lab. (PNNL)
  Effects of structural defects on the electrochemical activation of Li_2MnO_3.
- Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory,
  TXM studies of Li-rich materials as high energy density cathode materials for Li-ion batteries
- Johnson Control Inc.
  In situ XRD and XAS study of high Ni content high energy density cathode materials

- Beijing Institute of Physics, Chinese Academy of Sciences
  High energy density cathode material diagnostic studies using atomic level resolution STEM and in situ XRD and XAS
- Beijing Institute of Technology, Beijing, China.
  High-Rate and Cycling-Stable Li-Ion Batteries

Remaining Challenges and Barriers

- Morphology and elemental mapping of anode and cathode materials are needed as diagnostic tools for Li-ion battery research. The full field transmission x-ray microscopy (TXM) technique as well as micro- and nano- probe scanning TXM will be developed for battery research based on the high penetration power of x-ray beam at beamline at SLAC and APS, as well as new nano-probe beamline at NSLSII. High energy density anode and cathode materials will be studied using these new diagnostic tools and the combination of them to obtain the multi-length scale imaging and spectroscopy to provide valuable guidance for the new material developments.
- The In situ and ex situ diagnostic tools developed up today have been demonstrating their importance in understand the governing mechanism of performance and degradation of electrode materials for batteries. However, most of these studies are limited on the material level and the in situ techniques are mostly not under the real operating conditions. The disgnostic tools at operando conditions need to be developed and applied to the component (electrode) and cell and pack level.

Proposed Future Work for *FY 2016* and *FY2017*

- **FY2017 Q3 Milestone:**

Complete the XRD and XAS studies of $Li_2Ru_{0.5}Mn_{0.5}O_3$cathode material samples with different cycle history (charge and discharge limit and cycle numbers).

- **FY2017 Q4 Milestone:**

Complete the structure studies $Li_2Ru_{0.5}Mn_{0.5}O_3$, as a model compound for Li and Mn rich (LMR) high energy density cathode materials using scanning transmission electron microscopic (STEM) to correlate the voltage and capacity fading with micro-structural defects in this type of materials.

FY2017 work proposed:

- **The full field transmission x-ray microscopy (TXM) technique as well as micro- and nano- probe scanning TXM techniques will be developed and applied for Li-ion battery research. These techniques will be combined with STEM to have a multi-length scale Imaging and spectroscopy tool for battery material studies.**
- **The x-ray fluorescence microscopy (XFM) technique will be developed and applied for Li-ion battery research.**
- **The collaborative research with US academic research institutions and industrial partners will be further expanded and strengthened.**

Any proposed future work is subject to change based on funding levels.

Summary

- **Relevance**
  - ✓ *Diagnostics study aimed to improve the rate capability of batteries.*
  - ✓ *Diagnostics study of thermal abuse tolerance (to improve the safety characteristics).*
  - ✓ *Diagnostics study aimed to improve the calendar and cycle life of batteries.*
  - ✓ *Diagnostics study of electrode materials with lower cost potential.*
- **Approaches**
  - *Time resolved X-ray diffraction (TR-XRD) and mass spectroscopy (MS)*
  - *In situ x-ray diffraction and absorption spectroscopy*
  - *Pair distribution function (PDF) studies to obtain more detailed understanding of structural changes of cathode materials during multiple cycling.*
  - *Quick x-ray absorption spectroscopy*
  - *Full field as well as micro- and nano- probe scanning TXM*
  - *High resolution transmission electron microscopy (HR-TEM)*
- **Technical Accomplishments**
  - *Completed the studies of $Li_2Ru_{0.5}Mn_{0.5}O_3$, as a model compound for Li and Mn rich (LMR) high energy density cathode materials using TXM and pair distribution function (PDF) to correlate the voltage and capacity fading with micro-structural defects. The results were published on Nano Energy*
  - *Completed the study on microstructural defects created by prelithiation through comparison of the STEM images between pristine and prelithiated $Li_2Ru_{0.5}Mn_{0.5}O_3$. The effects of such microstructural defects on the voltage fading during cycling were studied and the results were published on Nano Letters.*
- **Proposed Future work**
  - *Continue and complete the PDF and STEM studies of $Li_2Ru_{0.5}Mn_{0.5}O_3$*
  - *Continue and complete the TXM studies of $Li_2Ru_{0.5}Mn_{0.5}O_3$*
  - *Develop and apply the XFM techniques for battery material studies*